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ADDITION OF t-BUTYL AND t-BUTYOXY RADICALS TO t-BUTYLISOCYANIDE. FRAGMENTATION PATTERNS IN RESULTING IMIDOYL RADICALS.

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Reports to date of free radical additions to isocyanides are rare as well as inconclusive. (2) Recently, we initiated a study of such reactions aimed at (i) assessing their generality, and (ii) their facility relative to other well-defined free radical reactions. We wish to report our initial findings now on the addition of t-butoxy and t-butyl radicals to t-butylisocyanide at 125°C.

In preliminary experiments, we observed that thermolysis of di-t-butylperoxide (DBP) (125°) in the presence of t-butylisocyanide led to formation of t-butylisocyanate and pivalonitrile presumably via the reactions below.

$$\underline{t}\text{-BuO}\cdot + \underline{t}\text{-BuNC} \xrightarrow{k_1} \underset{\mathbf{1}}{\underline{t}\text{-BuN=}\underset{\cdot}{\text{C}}\text{-OBu-}\underline{t}} \longrightarrow \underline{t}\text{-BuNCO} + \underline{t}\text{-Bu}\cdot \qquad (1)$$

$$\underline{t}\text{-Bu}\cdot + \underline{t}\text{-BuNC} \xrightarrow{k_2} \underset{\mathbf{2}}{\underline{t}\text{-BuN=}\underset{\cdot}{\text{C}}\text{-Bu-}\underline{t}} \longrightarrow \underline{t}\text{-BuCN} + \underline{t}\text{-Bu}\cdot \qquad (2)$$

The following competition experiment was designed to further elucidate these reactions. Reaction at 125°C of degassed and sealed Pyrex tubes containing variable conc. of isocyanide and cumene (as a competitive scavenger of t-BuO·) with 0.10 M DBP in chlorobenzene led to the product compositions in Table 1 after 15 min. This time period corresponds to 2-3% decomposition of DBP. We did our analysis at low conversion to product because of reaction between t-butylisocyanate and t-butyl alcohol at longer reaction times, and also because of the facile isomerization of isocyanide to nitrile that precludes pseudo-first order kinetics later in the reaction. Control experiments showed that all of the products are stable during the period of the reaction under study.

TABLE 1. PRODUCTS FROM THE REACTION OF VARIABLE *t*-BUTYLISOCYANIDE AND CUMENE WITH DI-*t*-BUTYLPEROXIDE (0.10 *M*) IN CHLOROBENZENE FOR 15 MINUTES AT 125°C.[a]

REACTANTS			PRODUCTS[b]				
t-BUTYL-ISOCYANIDE	CUMENE		*t*-BUTYL-ISOCYANATE	*t*-BUTYL ALCOHOL		ACETONE	PIVALONITRILE
M			m*M*			m*M*	
a	b	a/b	c	d	c/d		
0.0	2.22	0.0	0.0	1.78	0.0	1.73	0.0
2.02	4.94	0.41	0.94	1.87	0.50	0.86	62.8
3.65	3.37	1.08	1.47	1.58	0.93	1.29	191
3.59	2.38	1.51	1.73	1.40	1.23	1.19	249
4.30	2.02	2.12	1.90	1.08	1.75	1.39	367
6.16	2.24	2.75	2.06	0.83	2.48	1.22	547

[a] DBP has decomposed 2.8% after 15 min. at 125°.

[b] Product analyses were carried out by glc using an 11 ft, 20% TCEP on Chromsorb P column at 60°C, inj. port 100°C. Toluene was added to the samples before injection as an internal standard. Error limits ± 5%.

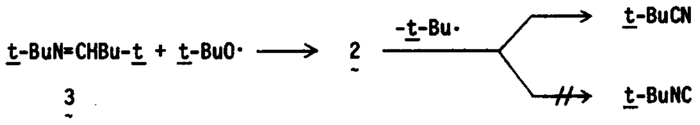
Analysis of a kinetic scheme including eqs 1 and 2 above and 3 and 4 below gives [*t*-BuNCO]/[*t*-BuOH]=(k_1/k_3)[*t*-BuNC]/[Cumene]. This relationship should hold under the pseudo-first order conditions of Table 1 where the concentrations of the competitive scavengers for *t*-BuO· do not change appreciably during the reaction. From the data in Table 1, (k_1/k_3) = 0.84 ± 0.16 so that *t*-butylisocyanide is comparable to cumene in its reactivity towards *t*-butoxy radical. Based on available kinetic data relevant to k_3 (2), we estimate $k_1 \approx 10^5$ M^{-1} sec^{-1} at 125°C.

$$t\text{-BuO}\cdot + \text{Cumene} \xrightarrow{k_3} t\text{-BuOH} + \text{Cumyl Radical} \qquad (3)$$

$$t\text{-BuO}\cdot \xrightarrow{k_4} \text{Acetone} + CH_3\cdot \qquad (4)$$

Table 1 shows that isomerization of *t*-butylisocyanide to pivalonitrile is facile and apparently is a chain process under our reaction conditions. Note that while only ca 3% of the added 0.10 *M* DBP has decomposed during the reaction period, the pivalonitrile yield ranges from 0.060 - 0.500 *M*. A control experiment showed that *t*-butylisocyanide is stable for extended periods at 125° in the absence of DBP. Thus eq 2 appears to "turn over" 10-100 times for each radical initiation step. Qualitatively, the turn over factor increases with increasing isocyanide concentration which is consistent with the free radical chain process.

The imidoyl radical **2** partitions only to pivalonitrile based on the following observation. Reaction of a mixture of imine **3** (1.5 *M*) and DBP (0.10 *M*) in chlorobenzene at 125°C leads to pivalonitrile but not isocyanide, even at very short reaction times corresponding to <1% DBP decomposition. This paritioning of 2 is consistent with the relative stabilities of isomeric isocyanide and nitrile structures since the heats of formation of the latter are more favorable by 15-25 kcal/mole. (4)



Recent epr (5) and other chemical evidence (6) supports the existence of imidoyl radicals. Further work is in progress on radical additions to isocyanides and the reactivity of the resulting imidoyl radicals.

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